938,699

PATENT SPECIFICATION

DRAWINGS ATTACHED

938,699

Date of Application and filing Complete Specification Dec. 16, 1960.
No. 43351/60.
Application made in Germany (No. S66308 IVa/12i) on Dec. 17, 1959.
(Patent of Addition to No. 809,250 dated May 17, 1955).
Complete Specification Published Oct. 2, 1963.

Index at acceptance:—Classes 1(2), AK10; and 82, I4A(2:3C:3X).

International Classification:—C01b (C22b).

COMPLETE SPECIFICATION

Improvements in or relating to Processes and Apparatus for the Production of Ultra-pure Semi-conductor Substances

We, SIEMENS & HALKSE AKTIENGESELLSCHAFT, a German Company of Siemensstadt, Berlin, Germany, and Wittelsbacher Platz 4, Munich 2, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to processes and apparatus for the production of ultra pure silicon or other semi-conductor substances. Processes in accordance with the invention constitute an improvement in or modification of the processes claimed in any of claims 1 to 3 of Patent Specification No. 809,250. In Claim 1 of the above mentioned Specification there is claimed a process for producing ultra-pure silicon or other ultra-pure semiconductor substances from the gaseous phase by chemical conversion, wherein the substance produced is precipitated from the gaseous phase onto a longitudinally extending carrier body consisting of the said substance or of a component of the said substance, wherein the carrier body is heated by an electric current flowing through it, and wherein the substance is precipitated along the length of the carrier body.

If the degree of purity of the reaction gas from which the substance, *e.g.* silicon is precipitated is sufficiently high, the silicon deposited has a degree of purity corresponding to that of the reaction gas and settles only on the highly heated carrier body provided that the other parts of the reaction arrangement do not heat up noticeably during the said process. In order to produce a carrier body of high quality it is important for the surface temperature of the carrier body to be adjusted to, and preferably maintained constant at, a certain value which depends on the kind of silicon compound being used and possibly also on the concentration thereof in the reaction gas. If the reaction gas consists of $SiHCl_3$ mixed with hydrogen in a preferred manner, (constant mol proportion $SiHCl_3:H_2$ approximately equal to 0.04) then the optimum surface temperature for the production of the silicon mono crystal is 1125° C. For this reason it has been proposed already that the surface temperature of the carrier be kept under constant observation and any changes of temperature which occur during the operation be balanced out by the operation of additional means which are inserted in the current circuit of the carrier, *e.g.* by means of a variable resistor.

This process was developed further in Patent No. 889,192 in which the resistance value of the carrier is reduced at the beginning of the process by pre-heating the carrier, or by reducing the degree of cooling thereof, at which value the operating current flowing through the carrier is capable, in spite of the strong cooling occurring during operation, of increasing or maintaining constant the temperature of the carrier.

The temperature of the carrier is then such that the voltage across the carrier body decreases with an increase in the operating current and this function is manifested in the "unstable region" of the current-voltage characteristics referred to in the latter mentioned Patent.

The aforesaid pre-heating of the carrier however results in relatively large energy losses since a considerable portion of the heat energy made available is delivered to the reaction vessel and the remaining parts of the apparatus adjacent thereto. Further, there is the danger present of foreign bodies

(impurities) evaporating from the heated portions of the apparatus, and possibly the reaction vessel, which impurities contaminate the deposited silicon. On the other hand the design and provision of means for reducing the heat radiation necessitate considerable technical skill and adds of course to the expense of the apparatus.

Finally, the provision of apparatus in which a high-voltage is produced which is sufficient to produce in the carrier body, which is highly resistive in the cold state, an electric current of such magnitude that the carrier is pre-heated to the required degree, is expensive and moreover cannot be readily utilised without danger.

Accordingly, it is an object of this invention to provide an improved process and apparatus for the production of ultra-pure semiconductor substances in which means are provided to enable the carrier to be heated to the degree necessary for deposition by the passage therethrough of current supplied from the normal operating current source.

The invention consists in a process for producing ultra-pure silicon or other ultra-pure semiconductor substances as claimed in any of Claims 1 to 3 in Patent Specification No. 809,250, wherein the conductivity of the carrier body is initially increased by subjecting the carrier body to radiation having a wave-length of between 1.1 and 12.10^{-3} microns, so that the said current flowing through the carrier body causes the temperature thereof to rise to such value that the voltage across the carrier body decreases with an increase in the current therethrough.

Preferably, the carrier body is irradiated uniformly along the whole length thereof with polychromatic visible light rays and infra-red rays. The polychromatic light rays may together constitute white light, *e.g.* light emitted from an electrically heated filament, whilst the operating current is applied, or the light rays may be monochromatic and have a wavelength not longer than 1.1 μ. In most cases a short irradiation for a duration of from one second to one minute is sufficient if a 500 Watt lamp or an even stronger lamp is spaced from the carrier by a distance of from 5 to 10 cm, and the voltage delivered by the operating current source and applied across the ends of the carrier is 500 V or more. Under certain circumstances it is possible to operate with ordinary mains voltage *e.g.* 220 V. The preferred voltage range is 220 to 500 volts. However, since the exposure time employed depends to a large degree on the radiating power of the lamp and its distance from the carrier body, the properties of the carrier, *e.g.* the specific resistance thereof and its surface recombination, and the voltage applied to the carrier, the exposure time may, of course, in individual cases deviate considerably from the above stated values.

In order to enable the carrier body to be irradiated as uniformly as possible over its whole length optical means, *e.g.* cylindrical concave mirrors or cylindrical lenses may serve to focus a quantity of the rays emitted from the filament on to the rod-like carrier body. It is not necessary for the carrier body to be irradiated over the whole circumference thereof. The radiation source and the optical focussing means are located outside the reaction vessel which must, of course, be transparent for the emitted rays.

The carrier body may be located in a transparent quartz vessel and the radiation focussed by means of a thermally-resistant body having a reflective concave surface, the filament being located between the vessel and the thermally-resistant body in such a manner that radiation emitted by the filament is reflected by the reflective surface of the thermally-resistant body.

Alternatively, in such an arrangement, the radiation may be focussed by a cylindrical lens located between and parallel to the filament and the carrier body.

Preferably, variable resistance means is provided to control the current through, and the temperature of, the carrier body. The temperature of the carrier body may be maintained constant at a point in the "unstable" region where the current-voltage characteristic of the resistance means is at a tangent to the current-voltage characteristic curve of the carrier body, as explained in Patent Specification No. 889,192, or it may be maintained constant at a point in the "unstable" region where the current-voltage characteristic of the resistance means cuts the current-voltage characteristic curve of the carrier body.

In order that the invention can be fully understood a preferred embodiment thereof will now be described with reference to the accompanying diagramamtic drawing, in which:—

Figure 1 is a part-sectional side elevation of an apparatus according to the invention; and

Figure 2 is a part-sectional plan view of the apparatus illustrated in Figure 1.

Details of the apparatus which are not necesary for an understanding of the invention have been omitted.

Referring now to Figures 1 and 2 a rod-like carrier body 1 of highly purified silicon which is to be thickened by a deposition process is held between two electrodes 2 and 2' in a cylindrical quartz reaction vessel 3 which completely encloses the carrier. The reaction gas, which contains the highly purified gaseous silicon compound (e.g. $SiHCl_3$) mixed, for instance, with hydrogen, enters the reaction vessel through an inlet port 4 and the spent gas leaves through an outlet

port 5. An operating current source 6, which together with the variable limiting resistor 7 determines the working point of the carrier body in the manner described in the aforesaid Patent No. 889,192, supplies the current for heating the carrier. A longitudinally extending radiation source 8, namely, an electrically heated filament, which is of approximately the same length as the carrier is arranged in a glass envelope outside the reaction vessel 3 and extends parallel to the carrier 1 so that the latter is irradiated as uniformly as possible along its whole length. A concave mirror-like reflector 9, shaped in the manner of a trough of part-elliptical cross-section and consisting of a thermally resistant material is located adjacent to the radiation source 8. This reflector, which is of approximately the same length as the radiation source 8 and the carrier 1 and is parallel thereto, partially surrounds the radiation source 8 and reflects and focusses the rays emitted from the source on to the carrier 1. The reflected rays are thus brought to a focus along a line coinciding with the axis of the carrier body, and this line will be referred to hereinafter as a "focal line" for convenience. Thus there are two focal lines associated with the reflector and parallel thereto which lines correspond with the focal points of an optical lens. Consequently, the radiation source, which is located along one of the two focal lines of the reflector throws its image upon the carrier since the latter is located along the other focal line. This is illustrated more clearly by ray paths drawn dash-dotted in Figure 2.

The wavelength of the light used when monochromatic radiation is employed must not be longer than 1.1 μ since rays having a longer wavelength are substantially unable to produce, photoelectrically, charge carriers in the silicon carrier body. On the other hand the depth of penetration decreases with increasing frequency so that the charge carriers produced are concentrated on the surface of the carrier body to an increasing degree as the wave-length decreases further, with the result that the number of charge carriers produced increases more slowly. If the recombination of the charge carriers at the surface of the carrier body is particularly strong it is advisable to use infra-red radiation, the wavelength of which is not longer than 1.1 μ, since these rays have a relatively large penetration depth and are therefore capable of producing the required number of charge carriers in the interior of the carrier body in which there is less recombination.

The application of monochromatic radiation however is, in general, unnecessary and polychromatic radiation may alternatively be used, in particular since a lamp emitting white light has a range of radiation including infra-red rays necessary for a deep penetration and rays of shorter wavelengths which effect the production of the charge carriers on the surface of the carrier body. Further, white light has the advantage in that it is simple to produce.

The invention may be applied with advantage even when the carrier body contains impurities manifesting *p-n* junctions, which junctions may be formed under certain circumstances in spite of the high purity of the melt in a "zone drawing" method of producing the carrier body.

WHAT WE CLAIM IS:—

1. A process for producing ultra-pure silicon or other ultra-pure semiconductor substances as claimed in any of Claims 1 to 3 in Patent Specification No. 809,250, wherein the conductivity of the carrier body is initially increased by subjecting the carrier body to radiation having a wave-length of between 1.1 and 12.10^{-3} microns, so that the said current flowing through the carrier body causes the temperature thereof to rise to such a value that the voltage across the carrier body decreases with an increases in the current therethrough.

2. A process as claimed in Claim 1, wherein the radiation consists of polychromatic visible light rays and infra-red rays.

3. A process as claimed in Claim 2, wherein the polychromatic light rays together constitute white light.

4. A process as claimed in Claim 1, wherein the radiation is monochromatic.

5. A process as claimed in Claim 3, wherein the radiation is emitted from an electrically heated filament.

6. A process as claimed in Claim 5, wherein the filament is longitudinally extending parallel to the carrier body, and wherein a quantity of the radiation emitted from the filament is brought to a focus along the whole length of the carrier body.

7. A process as claimed in Claim 6, wherein the carrier body is located in a transparent quartz vessel, and wherein the radiation is focussed by a thermally-resistant body having a concave reflecting surface, the filament being located between the vessel and the thermally-resistant body in such a manner that radiation emitted by the filament is reflected by the reflective surface of the thermally resistant body.

8. A process as claimed in Claim 6, wherein the carrier body is located in a transparent quartz vessel, and wherein the radiation is focussed by a cylindrical lens located between and parallel to the filament and the carrier body.

9. A process as claimed in any of Claims 1 to 8, wherein the carrier body is connected across a voltage source of from 220 to 500 volts.

10. A process as claimed in any of Claims 1 to 9, wherein variable resistance means is

provided to control the current through, and the temperature of, the carrier body.

11. A process as claimed in Claim 10, wherein the temperature of the carrier body is maintained constant at a point where the current-voltage characteristic of the resistance means is at a tangent to the current-voltage characteristic curve of the carrier body.

12. A process as claimed in Claim 10, wherein the temperature of the carrier body is maintained constant at a point, where the current-voltage characteristic of the resistance means cuts the current-voltage characteristic curve of the carrier body.

13. A process as claimed in any of Claims 1 to 12 wherein the carrier body consists of silicon and the reaction gas is silicochloroform ($SiHCl_3$).

14. A process as claimed in any of Claims 1 to 13, wherein the reaction gas is mixed with hydrogen.

15. A process of producing ultra-pure semiconductor substances substantially as herein described with reference to the accompanying drawing.

16. Semiconductor substances produced by a process as claimed in any of Claims 1 to 15.

17. Apparatus for carrying out a process as claimed in any of Claims 1 to 15, substantially as herein described with reference to the accompanying drawing.

For the Applicants,
G. F. REDFERN & CO.,
St. Martin's House, 177, Preston Road,
Brighton, Sussex.

Leamington Spa: Printed for Her Majesty's Stationery Office by the Courier Press.—1963.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2. from which copies may be obtained.

938699 COMPLETE SPECIFICATION
1 SHEET *This drawing is a reproduction of the Original on a reduced scale*

Fig.1

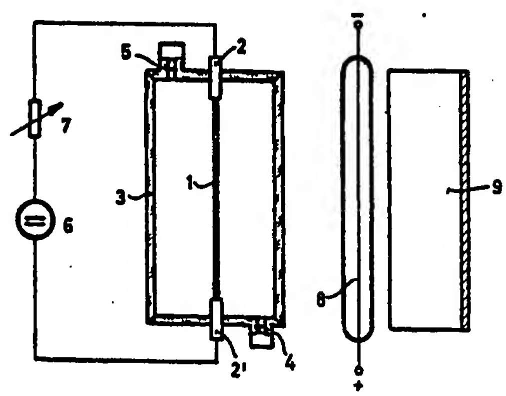

Fig.2